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(54) Composition for disinfecting and for inhibiting scale

(57) An aqueous composition having a pH of more than 9 consists of a stabilized chlorine dioxide precursor, an alkali metal polyphosphate and an alkali metal hydroxide. The stabilized chlorine dioxide precursor is a solution comprising sodium chlorite/chlorate stabilized with sodium carbonate. The polyphosphate contains a mixture of dimer and other polyphosphates having an average 'polymer' length equivalent to a tetramer. The alkali metal hydroxide includes KOH, NaOH and NH_4OH. The method of forming the solution involves adding the alkali metal hydroxide to a solution of the polyphosphate in order to raise the pH, adding the chlorine dioxide precursor and adding additional alkali metal hydroxide to raise the pH to above 9. In use, an acid such as HCl, H_3PO_4 or citric acid is added to the solution to lower the pH to less than 7 and the solution is then injected into the water to be treated. The composition acts as a disinfectant, threshold scale inhibitor and corrosion inhibitor.

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TREATMENT OF WATER IN WATER DISTRIBUTION SYSTEMS

The present invention relates to a chemical formulation containing a polyphosphate and chlorine dioxide for the treatment of water in water distribution systems.

The responsibility for the quality of water passes from the water supply company to the user once the water passes into the user's premises. In buildings containing large water distribution systems, such as hotels, hospitals or leisure complexes, maintaining the quality of water at the required level is difficult. The quality of water is influenced by the following factors:

1) Micro-biological fouling, including bio-film;
2) Deposition of scale by hard water; and
3) Corrosion of ferrous metal pipework resulting in "red water".

These problems have both financial and health and safety implications.

The government have laid down a health and safety guideline HS(G)70 and an accompanying Approved Code of Practice which are concerned with the control of Legionellosis including Legionaires disease, which is spread through contaminated water systems.

There are two methods currently used to control microbiological growth, both are approved by HS(G)70. The first, being a temperature control wherein cold water should be stored and distributed at or below 20°C and hot water should be stored at 60°C and distributed at 50°C after the tap has been running for 1 minute. Old systems and those which are

required to meet certain design criteria cannot maintain this degree of temperature control. The second control method uses 2mg/L of free chlorine, however this can impart a taste to the water as well as increasing the production of trihalomethanes and trichlorophenols. Furthermore its efficiency is greatly reduced at a pH of more than 8; in the UK it is not unusual to have water at a pH of 8 - 8.5 especially where base exchange softening is used.

The most common known form of scale control is to use base exchange softening which exchanges magnesium and calcium in water entering the system for sodium, therefore softening the water. The problems associated with this method are a level of sodium which may be above that permitted for human consumption as well as the production of a more corrosive water. Additionally substantial amounts of sodium carbonate are produced which decomposes when heated to yield sodium hydroxide causing a pH rise sufficient to cause the degradation of chlorine dioxide to chlorite and chlorate therefore reducing its efficacy as a secondary disinfectant.

To maintain the quality of water in public and other buildings it is known to use, separately, chlorine dioxide to control microbiological growth and a polyphosphate as a scale inhibitor in two separate dosing operations which is expensive both initially and in terms of maintenance and involves complex monitoring.

Chlorine dioxide is known to have advantages over free chlorine, it does not impart a taste to the water, reduces the chance of forming toxic chemicals and is efficient over a wider pH range. Polyphosphates are known to be effective as threshold scale inhibitors.

Sodium polyphosphate solution and stabilized chlorine dioxide precursor solution, containing a chlorite such as sodium chlorite are, readily available separately but cannot be combined by direct mixing. Such chlorine dioxide precursor solutions are only stable at concentrations of up to 5% available chlorine dioxide and pH 10. Sodium polyphosphate has a pH of below 7, therefore if the chemicals are mixed the chlorine dioxide precursor will destabilize and active chlorine dioxide will be evolved. At pH 10 polyphosphate solutions hydrolyse to form orthophosphates and the scale inhibiting properties are lost.

There are few methods used to limit corrosion. Storage tanks may be lined with a corrosion resistant substance; however pipes are, in general, unprotected. This can result in "red-water" from contamination by ferrous pipes.

With the above problems in mind we have now developed a chemical formulation which is designed:-

1) to act as a primary disinfectant for the control of bacteriological contamination, including Legionella pneumophilia;

2) to act as a secondary disinfectant to maintain control of bacteria within the system and to remove and further prevent the formation of bio-film;

3) to act as an efficient "threshold" scale inhibitor to control the deposition of hardness scale throughout the system and particularly in areas of high heat flux such as calorifiers, boilers and other heat exchangers; and

4) to act as a multi-metal corrosion inhibitor throughout the system and, where necessary, preventing the formation of red-water.

Accordingly from one aspect the present invention provides an aqueous chemical composition comprising stabilized chlorine dioxide precursor, an alkali metal polyphosphate and an alkali metal hydroxide, the composition having a pH of greater than 9 and wherein the alkali metals are preferably not the same.

In the present description the term "alkali metal" is intended to include ammonium.

The stabilised chlorine dioxide precursor is preferably a solution comprising sodium chlorite with sodium carbonate as the stabiliser. A 30% solution containing 10% $^{w}/_{v}$ sodium carbonate is especially suitable.

Preferably the alkali metal polyphosphate is sodium polyphosphate. A suitable commercially available sodium polyphosphate is a mixture of dimer and other polyphosphates having an average "polymer" length equivalent to a tetramer.

Preferably the pH of the composition is in the range of 9.4 - 9.8.

The composition of the present invention eliminates the need to use base exchange softening which in turn maintains the sodium content of the water at its original level which in turn maintains the original levels of calcium and magnesium in the water thus producing a lower Ryznar Stabilility Index and reducing the risk of corrosion. The product also controls the proliferation of bacteria and bio-film. The advantages of using chlorine dioxide in place of free chlorine have been mentioned above.

According to a second aspect the present invention provides a method of providing a stable aqueous solution containing a chlorine dioxide precursor and an alkali metal polyphosphate comprising raising the pH of an aqueous solution of an alkali metal polyphosphate to greater than 8 by the addition of an alkali metal hydroxide, adding stabilized chlorine dioxide precursor solution and adjusting the pH to greater than 9 by the addition of further alkali metal hydroxide and wherein the alkali metal in the polyphosphate is sodium the metal in the hydroxide is different.

The pH may be adjusted using ammonium hydroxide or an alkali metal hydroxide.

Where sodium polyphosphate is the scale control the pH is preferably adjusted using potassium hydroxide.

Since both the stabilized chlorine dioxide and sodium polyphosphate solutions contain high levels of sodium ions, any further addition of sodium ions, e.g. from sodium hydroxide used to adjust the pH would cause precipitation of the polyphosphates owing to the common ion effect.

The composition is stable at 4 - 20°C for up to 6 months.

According to a third aspect the present invention provides a method of treating water in a water distribution system comprising the addition of an acid activator to the composition of the present invention to reduce the pH to less than 7 and injecting the aqueous solution to the water system. The preferred acid activator is hydrochloric acid although other acids such as phosphoric or citric acid may be employed.

Only small volumes, 50 - 100 ml of the product need to be activated at a time preferably on a continuous basis, the volume of 50 - 100 ml acting as a buffer stock.

The time between activation and injecting must be short as long term contact of the polyphosphate with an acid causes degradation to the orthophosphate; preferably injection occurs immediately following the addition of the acid activator.

The following example illustrates the present invention.

A 30% $^{w}/_{v}$ sodium chlorite is prepared from 70% commercial sodium chlorite containing 10% $^{w}/v$ sodium carbonate.

To 12L of 20% $^{w}/_{v}$ sodium polyphosphate is added, at ambient temperature, 2.5L of 32% $^{w}/_{v}$ potassium hydroxide solution followed by 5.4L of 30% $^{w}/_{v}$ sodium chlorite solution. The pH of the solution is adjusted to about 9.5 by the addition of further 32% potassium hydroxide solution.

The resultant solution is stable at ambient temperatures and has a shelf life of up to about 6 months.

In use in the disinfection of water in distribution systems the above solution is continuously metered into an enclosed holding vessel of 50 ml capacity simultaneously with a 3% $^{w}/_{v}$ hydrochloric acid activator solution to release chlorine dioxide into solution. The resulting solution is continuously injected via a suitable injection means into the water system. The flow rates of the precursor solution, acid activator solution and

chlorine dioxide containing solution are adjusted with respect to the flow rate of the water in the system to treat $40m^3$ of water per 1L of precursor solution at levels of polyphosphate and chlorine dioxide concentrations that meet the Drinking Water Inspectorate levels.

As the two components, i.e. the precursor solution and the acid activator, are combined to form a "one-pack" product in the present invention only one set of injecting equipment is required which represents a saving on initial expenditure and maintenance costs; it also reduces the handling of chemical solutions.

While chlorine dioxide can act as a highly effective primary disinfectant during degradation its main use is as a secondary disinfectant. In order to be a highly effective secondary disinfectant it is important to slow down the degradation so that chlorine dioxide is maintained at a sufficiently active level throughout the distribution system. The present invention has the added advantage that the chemical formulation provides synergistic stabilisation of the active chlorine dioxide as the presence of phosphate at the time of activation and subsequently reduces the rate of degradation.

An additional advantage of the present invention lies in the relative ease that the chlorine dioxide, chlorate and chlorite concentrations, expressed as chlorine dioxide can be determined.

While chlorine dioxide, chlorite and chlorate can be accurately determined in the laboratory, chlorite and chlorate are more difficult to determine with field test equipment. However, phosphates are more easily determinable and as the product balance is initially known a further chemical control parameter for monitoring dosage, i.e. the total chlorine

dioxide, chlorite and chlorate can be determined from a total phosphate determination.

CLAIMS

1. An aqueous chemical composition comprising stabilized chlorine dioxide precursor, an alkali metal polyphosphate and an alkali metal hydroxide, the composition having a pH of greater than 9.

2. The aqueous chemical composition according to claim 1 wherein the alkali metals are not the same.

3. The aqueous chemical composition according to claim 1 or claim 2 wherein the stabilised chlorine dioxide precursor is a solution comprising sodium chlorite stabilised with sodium carbonate stabilised.

4. The aqueous chemical composition according to claim 3 wherein the solution comprises 30% $^{w}/_{v}$ sodium chlorite containing 10% $^{w}/_{v}$ sodium carbonate.

5. The aqueous chemical composition according to any preceding claim wherein the alkali metal polyphosphate is sodium polyphosphate.

6. The aqueous chemical composition according to claim 5 wherein the sodium polyphosphate is a mixture of dimer and other polyphosphates having an average "polymer" length equivalent to a tetramer.

7. The aqueous chemical composition according to any preceding claim wherein the pH of the composition is in the range of 9.4 - 9.8.

8. The aqueous chemical composition according to any one of claims 1 to 7 substantially as described herein.

9. A method of providing an aqueous chemical composition containing a chlorine dioxide precursor and an alkali metal polyphosphate comprising raising the pH of an aqueous solution of an alkali metal polyphosphate to greater than 8 by the addition of an alkali metal hydroxide, adding stabilized chlorine dioxide precursor solution and adjusting the pH to greater than 9 by the addition of further alkali metal hydroxide.

10. The method according to claim 9 wherein the alkali metal in the polyphosphate is sodium and the metal in the hydroxide is different.

11. The method according to claim 9 or 10 wherein the pH is adjusted using ammonium hydroxide.

12. The method according to any one of claims 9 to 11 wherein the pH is adjusted using potassium hydroxide.

13. The method according to any one of claims 9 to 12 substantially as described herein.

14. A method of treating water in a water distribution system comprising the addition of an acid activator to the composition according to any one of claims 1 to 8 to reduce the pH to less than 7 and injecting the aqueous solution in to the water system.

15. The method according to claim 14 wherein the acid activator is hydrochloric acid, phosphoric acid or citric acid.

16. The method according to claim 14 or claim 15 wherein 50 - 100 ml of the product is activated at a time, the volume of 50 - 100 ml acting as a buffer stock.

17. The method according to any one of claims 13 to 16 wherein the product is activated on a continuous basis.

18. The method according to any one of claims 13 to 17 wherein injection occurs immediately following the addition of the acid activator.

19. The method of treating water in a water distribution system according to any one of claims 14 to 18 substantially as described herein.

The Patent Office

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Claims searched: 1-19

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Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): A5E (EH, ET); C1C (CACE, CACG)

Int Cl (Ed.6): A01N 25/00; C02F 1/50, 1/76, 5/04, 5/08, 9/00

Other: Online: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X	US 4512908	(ECONOMICS LABORATORY, INC) See column 2 lines 33-37 & 53-54 and column 10 lines 1-18	1 at least
X	JP 63261000 & WPI Abstract Accession No. 88-349739	(LION HYGIENE KK) See abstract	1
X	KR 8902542 & WPI Abstract Accession No. 90-169466	(HWANG) See abstract	1 at least

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